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ELECTRICAL AND MAGNETIC PROPERTIES

Magnetic and Magnetocaloric Properties of $(MnCo)_{1-x}Ge$ Compounds

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Abstract—The crystal structure, magnetic properties, and heat capacity of the $(MnCo)_{1-x}Ge$ compounds with $x \le 0.05$ have been studied. It was found that, as the deviation from the MnCoGe stoichiometric composition increases, the temperature of structural transition from the low-temperature phase with the orthorhombic TiNiSi-type structure to the high-temperature phase with the hexagonal Ni_2In-type phase decreases rapidly, whereas the magnetic ordering temperature varies slightly. The temperature of structural transition for the composition with $x = 0.02$ approximately coincides with the Curie temperature of the hexagonal phase, and the transition is accompanied by a significant entropy change, namely, $\Delta S = 34$ J/(kg K). The application of high magnetic field in the transition-temperature range causes an increase in the relative volume of the orthorhombic phase. An analysis of magnetocaloric properties of these compounds, which was performed with the formal application of the Maxwell's relationship near the temperature of first-order structural phase transition, is shown to give overestimated values of the entropy change.

Keywords: intermetallic compounds, structural transition, X-ray diffraction, heat capacity, magnetocaloric effect

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INTRODUCTION

Magnetocaloric properties of magnetically ordered compounds in the range of phase transitions are the matter of active studies [1, 2]. This is related to both the investigation of the thermodynamics of phase transitions in magnetic materials and the search for new working materials for magnetic refrigerators. In particular, high entropy changes upon structural and first-order magnetic phase transitions were found for the $Gd_5(Si_{1-x}Ge_x)_4$ [3], Ni_2MnGa [4], $LaFe_{13-x}Si_x$ [5], and Mn(As, Sb) [6].

Recently, studies of magnetocaloric properties of MnCoGe-based compounds have been heavily emphasized [7, 8]. At high temperatures, the stoichiometric MnCoGe compound has a hexagonal (H) crystal structure of the Ni_2In type. As the temperature decreases to 453–470 K, the diffusionless first-order structural martensitic transformation to the orthorhombic TiNiSi-type structure takes place [9]. Variations in the composition allow one to change the temperature of structural transition [9, 10]. At low temperatures, both modifications are ferromagnetic, but their magnetizations and Curie temperatures (T_C) differ substantially [11, 12]. According to the calculations performed in [13], vacancies in the Co subsystem play a significant role in the stability of structural states of the compounds. High entropy changes in low magnetic fields, which are comparable to those for pure Gd, were found for the nonstoichiometric $MnCo_{0.95}Ge_{1.14}$ compound [14] upon magnetostructural transformation.

Previously, when studying the $Mn_{1.9-x}Co_xGe$ single crystals (with $0.8 \le x \le 1.65$) with an H structure, we found that the system demonstrates the spin-reorientation transition at $x = 0.95$ [12]. The compound containing equal Mn and Co amounts has the minimum magnetic anisotropy and, therefore, shows the most promise as a working body for magnetic refrigerators. Only a few percent of vacancies induced in the 3*d* subsystem of the $(MnCo)_{1-x}Ge$ compounds lead to the decrease in the structural-transition temperature by tens degrees and even to the complete suppression of the structural transition [15].

The aim of present study is to investigate the magnetic properties and heat capacity of the $(MnCo)_{1-x}Ge$ system with $x \le 0.05$, as well as the entropy change upon isothermal magnetization and temperature change during adiabatic magnetization in the range of structural-transition temperatures.

EXPERIMENTAL

The $Mn_{1-x}Co_{1-x}Ge$ alloys with $x = 0.01$, 0.015, 0.02, 0.03, 0.035, and 0.05 were melted in an argon atmosphere using an induction furnace and starting components of no less than 99.98% purity. The prepared alloys were annealed in an argon atmosphere at 850°C for 1 week.

The X-ray diffraction analysis of powder samples was performed at temperatures of 77–320 K using a DRON diffractometer and Cr $K\alpha$ radiation. The temperature and field dependences of magnetization were measured in fields of up to 7 T using a MPMS-XL-7 EC SQUID magnetometer and in fields of up to 1.6 T at temperatures of 4.2–320 K using a vibrating-sample magnetometer. Magnetization curves were measured in high pulsed magnetic fields with a pulse duration of 8 ms using the induction technique. The structural transformation is accompanied by substantial changes in the lattice volume, which result in the spontaneous destruction of samples and the formation of powder with a particle size of ~50 μm. Thus, all magnetic measurements were performed using powder samples. In order to avoid the rotation of individual particles in applied magnetic fields, the powders were compacted. To plot the dependences of magnetization in an internal magnetic field, data on the magnetization of powder Ni sample with both an analogous shape and particle size were used. The Curie temperature magnitudes were determined using the Belov–Arrote procedure and M^2 vs H/M dependences.

The heat capacity was measured using a low-temperature calorimeter in which the classic adiabatic method and a temperature-increase regime were applied. The adiabatic temperature change in an applied magnetic field was determined using direct measurements with differential thermocouples. A sample was placed between electromagnet poles, and the spacing was evacuated to a residual pressure of 10^{-3} Torr. The temperature was measured using a thin copper/constantan thermocouple with a wire diameter of 0.05 mm; the thermojunction was placed in the center of the sample. To check the correctness of the method, measurements were performed for the bulk Gd sample and bulk and powder $(MnCo)_{1-x}Ge$ ($x = 0.03$) samples. The relative error of the measurements is ±10%.

RESULTS AND DISCUSSION

Study of Sample Structure

X-ray diffraction studies performed at room temperature showed that the annealed $(MnCo)_{1-x}Ge$ alloys with $x < 0.05$ are single-phase. X-ray diffraction patterns of the compounds with $x \geq 0.035$ are typical of the hexagonal modification with the Ni_2In-type structure. No spontaneous structural transitions are observed for the compound at temperatures of 77–320 K. At low temperatures, the compositions with $x = 0.03$, 0.02, and 0.01 have the orthorhombic structure of the TiNiSi type. Upon heating, the compounds with $x = 0.03$, 0.02, and 0.01 exhibit the O → H structural transition at 205–225, 270–290, and 300–350 K, respectively. Figure 1a shows X-ray diffraction patterns taken for the composition with $x = 0.02$ upon heating at different temperatures in the range of structural transition. It is seen that, as the temperature increases, the intensities of reflections of the low-temperature O phase decrease, whereas the intensities of reflections of the high-temperature H phase increase. The both phases coexist in the range of structural transition. The relative volume of the H phase (ω_H) in the range of structural transition was determined using changes in integral intensities of X-ray diffraction reflections (Fig. 1b). The transformation of the crystal structure of the main portion of sample is observed within a narrow temperature range of about 12 K.

Figure 1c shows temperature dependences of the unit-cell volume of the O phase and double unit-cell volume of the H phase. It is seen that the structural transformation is accompanied by substantial—to 4%—volume change. Earlier [9, 16], the analogous volume change was observed upon structural transition in compounds of close compositions.

Magnetic Phase Diagram

Figure 2 shows the temperature dependences of spontaneous magnetization M_s determined from magnetization curves measured for the $(MnCo)_{1-x}Ge$ compounds at different temperatures. The existence of the structural transition in the compounds with $x = 0.03$, 0.02, and 0.01 leads to the appearance of anomalies in the $M(T)$ temperature dependences, which are accompanied by hysteresis. The Curie temperatures of the H phase in the compounds with $x = 0.035$ and 0.03 coincide and are 278 K. The Curie temperature of the H phase in the compound with $x = 0.02$ cannot be determined using our data; however, it follows from Fig. 2 that the spontaneous magnetization becomes zero at temperatures between 283 and 295 K.

At low temperatures, the compounds with $x = 0.01$, 0.02, and 0.03 have an orthorhombic structure. The temperature dependences of the magnetization of the compounds almost coincide in the temperature range of 4.2–200 K. Similarly, the composition with $x = 0.035$ and 0.03, which have a hexagonal structure, exhibit similar $M_s(T)$ dependences at the temperatures of 240–280 K. The composition with $x = 0.02$ exhibits an abrupt change in magnetization in the temperature range of the O → H structural transition (270–290 K). Simultaneously, the relative volume of H phase changes abruptly within the same temperature range. Using the relative volume (see Fig. 1b) and M_s magnitudes for the phases coexisting in the sample with $x = 0.02$, the expected change of magnetization in the range of structural transition temperatures can be easily calculated (filled triangles in Fig. 2). As can be

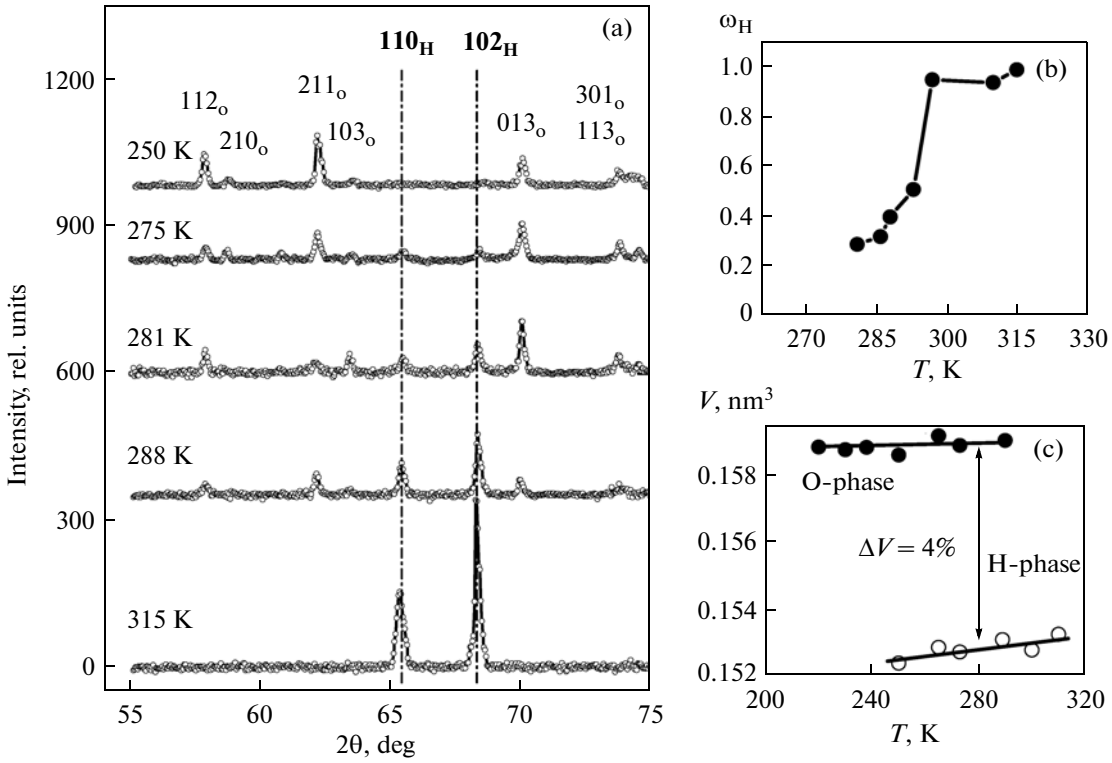

Fig. 1. (a) X-ray diffraction patterns taken with increasing temperature in the range of structural transition for the $(MnCo)_{0.98}Ge$ compound; (b) temperature dependence of the relative volume of hexagonal phase; (c) temperature dependences of unit-cell volumes of orthorhombic and hexagonal phases.

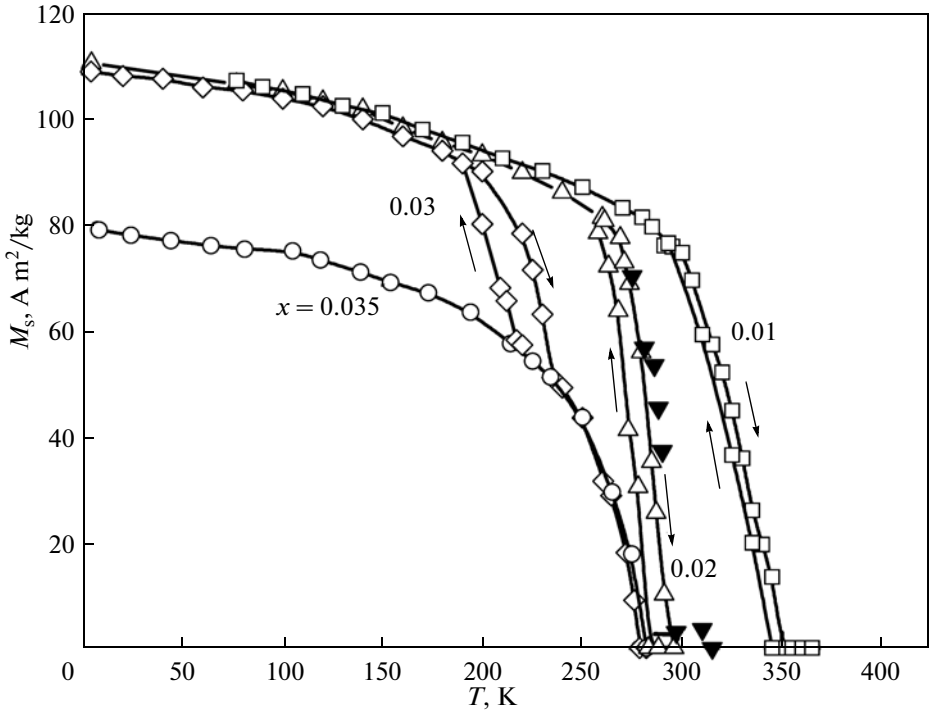

Fig. 2. Temperature dependences of the spontaneous magnetization of the $(MnCo)_{1-x}Ge$ compounds with $x = 0.035$, 0.03, 0.02, and 0.01. Filled triangles correspond to magnitudes obtained in allowing for the X-ray diffraction data on the amount of hexagonal phase.

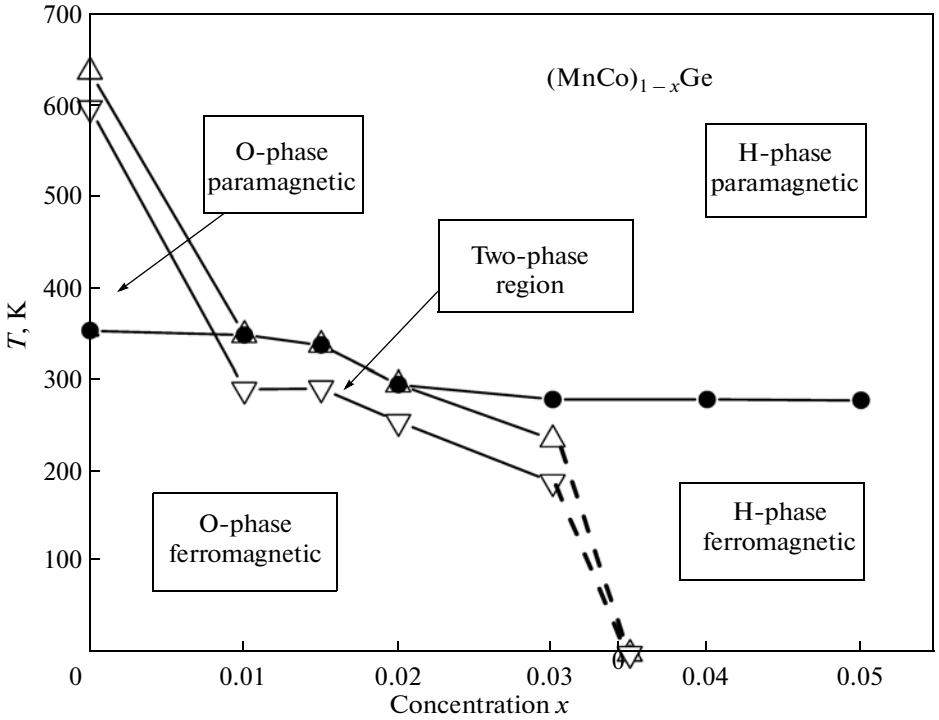

Fig. 3. Phase diagram of the $(MnCo)_{1-x}Ge$ system. Circles indicate temperatures corresponding to zero spontaneous magnetic moment. Triangles indicate regions of structural transformations; data for the MnCoGe compound (with $x = 0$) are taken from [16].

seen, the results agree adequately with data obtained by direct measurements. Thus, the change in the relative volume of phases is the cause for the decrease in the spontaneous magnetization of $(Mn–Co)_{0.98}Ge$ upon the O → H structural transition.

The results of magnetic measurements at different temperatures were used to plot the phase diagram of the $(MnCo)_{1-x}Ge$ system (Fig. 3). Upright triangles in Fig. 3 indicate the temperature of the disappearance of O phase in the course of heating, whereas inverse triangles indicate the temperature of disappearance of H phase in the course of cooling. Circles indicate temperatures at which the spontaneous magnetization of sample becomes zero. The temperatures of structural transition for the compounds with $x > 0.02$ are higher than the Curie temperature of the H phase; the disappearance of spontaneous magnetization is determined by the disappearance of the ferromagnetic O phase. It can be seen that, as the number of vacancies in the 3*d* sublattice increases, the T_C value decreases slightly, whereas the temperature of structural transition decreases abruptly.

Effect of Magnetic Field on Structural Transition

The magnetization of the orthorhombic phase exceeds substantially that of the hexagonal phase. Therefore, the magnetic field can increase the stability range of the O phase via shifting the temperature of structural transfition and can cause an increase in the volume of the O phase in the transition range. Previously [17], it was shown by magnetic measurements and X-ray diffraction studies performed in magnetic fields that the magnetic field applied to the $Mn_{1.07}Co_{0.92}Ge$ compound in the range of its structural transition leads to an increase in the volume of the O phase. The field-induced structural transition is irreversible, and the field dependence of magnetization exhibits hysteresis.

We measured the temperature dependences of magnetization in different fields in detail. Figure 4 shows some of the results. As the indicator of the temperature of martensitic transformation, we use A_s (austenite start), which is the temperature of the start of the O → H structural transition upon heating, which was determined using the second derivative of the $M(T)$ dependence. The inset in Fig. 5 shows the field dependence of the A_s temperature. It can be seen that a magnetic field of less than 2 T hardly changes the A_s temperature. In fields of 3–7 T, the A_s temperature increases linearly with increasing field, and the dA_s/dH magnitude is 1 K/T.

Studies of the magnetization of the composition with $x = 0.02$ at a fixed temperature in the range of structural transition shows that the magnetization curves exhibit no hysteresis in magnetic fields of below 2 T. The difference between the ascending and descending branches of hysteresis loops appears after magnetization in fields of above 2 T. Thus, a field of ~2 T is the threshold; when magnetizing in lower

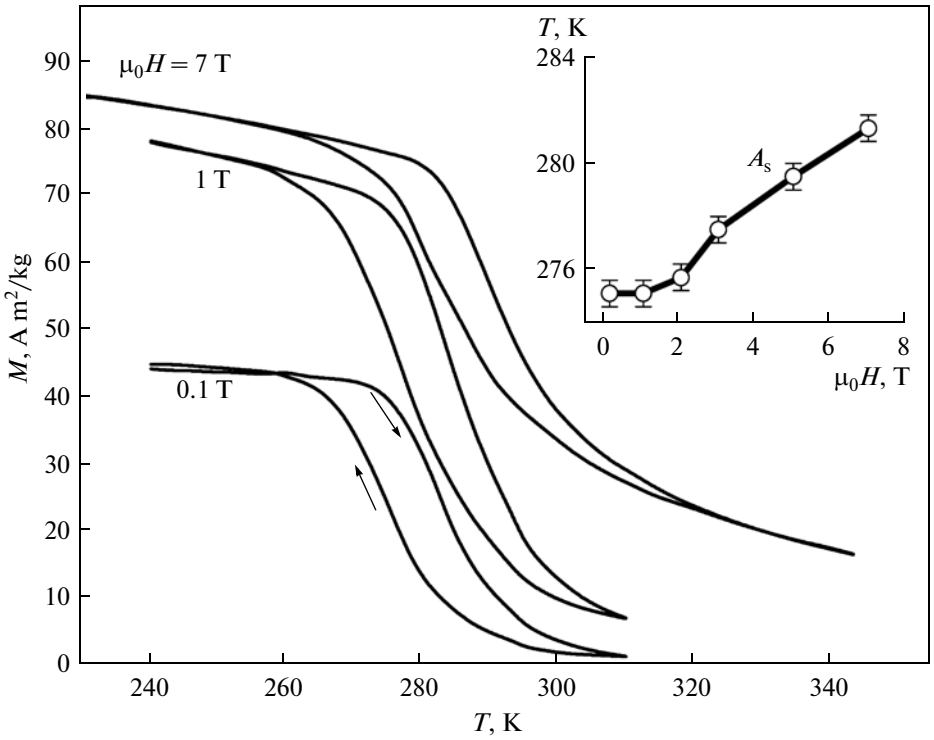

Fig. 4. Temperature dependences of the magnetization of the $(MnCo)_{0.98}Ge$ compound measured in different fields. The inset shows the field dependence of the temperature on the onset of structural transformation (A_s) upon heating.

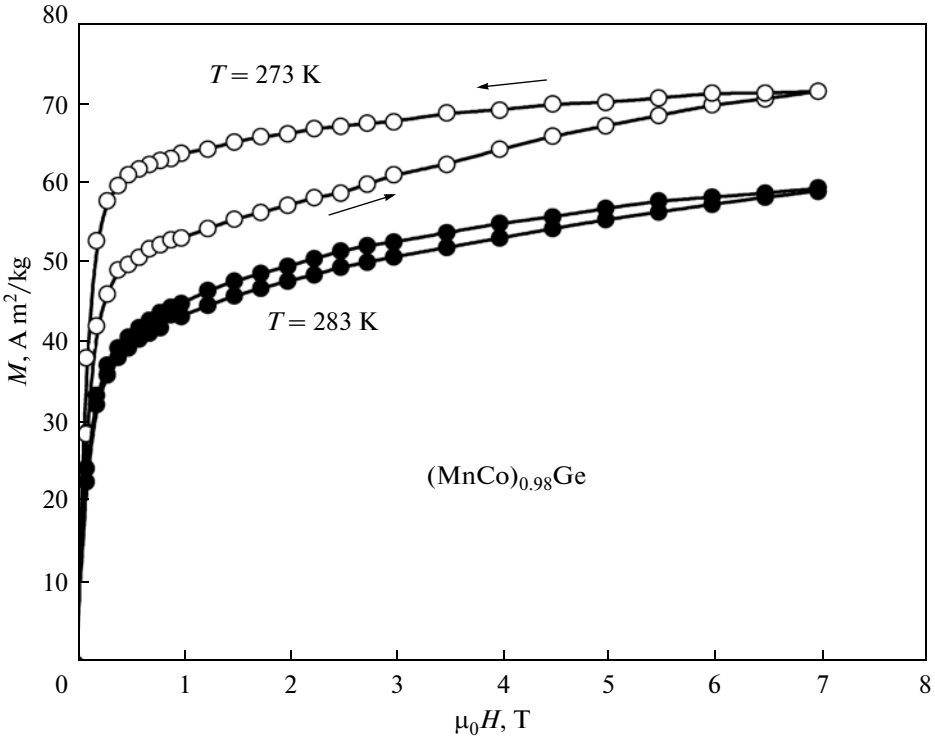

Fig. 5. Field dependences of the magnetization of the $(MnCo)_{0.98}Ge$ compound measured (with the SQUID magnetometer) after (●) heating to 283 K and (○) cooling to 273 K.

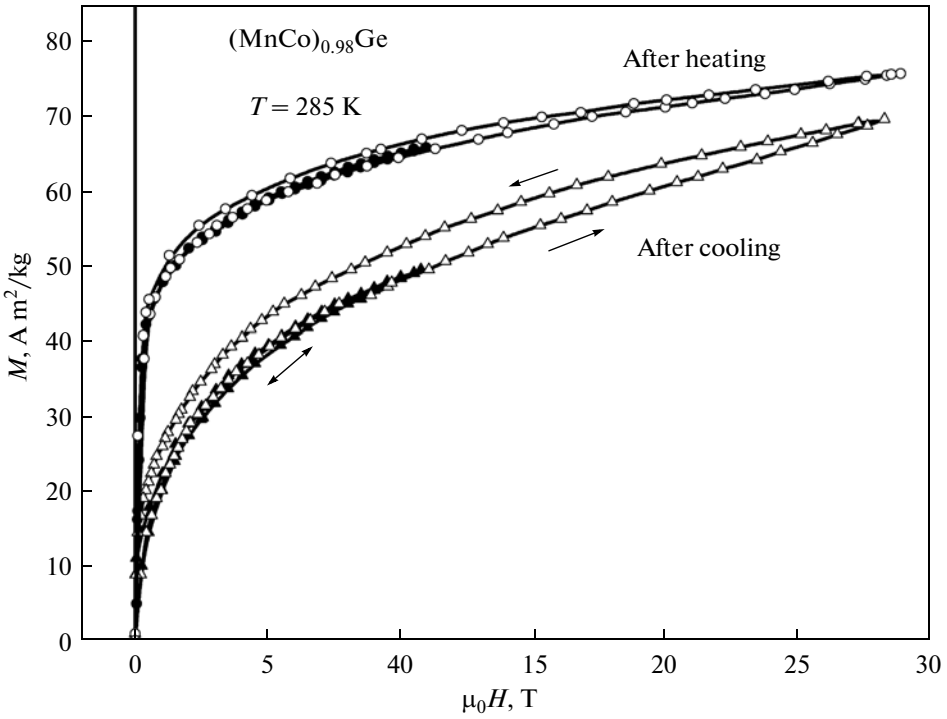

Fig. 6. Field dependences of the magnetization of the $(MnCo)_{0.98}Ge$ compound measured in pulsed fields after (○) heating to 285 K and (△) cooling to 285 K.

fields, the relative amount of coexisting O and H phases is unchanged, and the isothermal magnetization is a reversible process.

Figure 5 shows two field dependences of magnetization of the $(MnCo)_{0.98}Ge$ sample at fixed temperatures. The first dependence was obtained after heating in a range of from 240 K (the starting temperature) to 283 K (the measuring temperature), which approximately corresponds to the middle of O → H structural transition. The second curve was measured after cooling in the range from 350 to 273 K, which is close to the middle of the reverse H → O transition. It can be seen that, in the first case, the applied magnetic field slightly changes the volume fractions of the O and H phases in the sample, whereas, in the second case, approximately 20% of the orthorombic phase is induced. Causes for this asymmetry are discussed in detail by an example of the Ni_2MnGa compound [18].

The field-induced martensitic transformations are diffusionless and can occur very rapidly. The time required for the occurrence of field-induced martensitic transformation in the Fe–Ni–Mn alloy is 20 μs [19]. At the same time, the amount of martensite induced upon applying a dc field was found to be markedly higher than that of martensite induced by pulsed fields with durations of several dozen milliseconds [20]. The magnetic shape-memory effect is due to the field-induced displacement of twin boundaries in the martensitic phase. This process occurs completely for about 250 μs [21]; this allows for the pulsed magnetization or ac field (to 2 kHz in frequency) systems to be used.

Figure 6 shows magnetization curves measured for the $(MnCo)_{0.98}Ge$ compound at 285 K in pulsed magnetic fields with pulse durations of 8 ms. After heating from a starting temperature of 240 K, the sample before magnetization is mainly in ferromagnetic state and has the orthorhombic structure (circles). At the same time, after cooling from 350 K, the paramagnetic phase with the hexagonal structure (triangles) dominates in the sample. In both cases, the magnetization curves measured in fields of to 11 T (filled symbols) are hysteresisless in contrast to the curves measured in static fields (Fig. 5). Curves measured upon applying fields up to 29 T exhibit a slight hysteresis that is more substantial in curves measured after cooling. Thus, the field-induced martensitic transformation in MnCoGe is accompanied by relaxation processes. This fact indicates the existence of a high potential barrier between the energies of orthorhombic and hexagonal phases. This agrees adequately with the existence of the experimentally observed threshold field.

Heat Capacity and Magnetocaloric Properties

Figure 7a shows the temperature dependences of the heat capacity C_P for the compositions with x = 0.02, 0.03, and 0.035. It can be seen that the martensitic transformations are accompanied by substantial anomalies in the dependencies. Figure 7b shows tem-

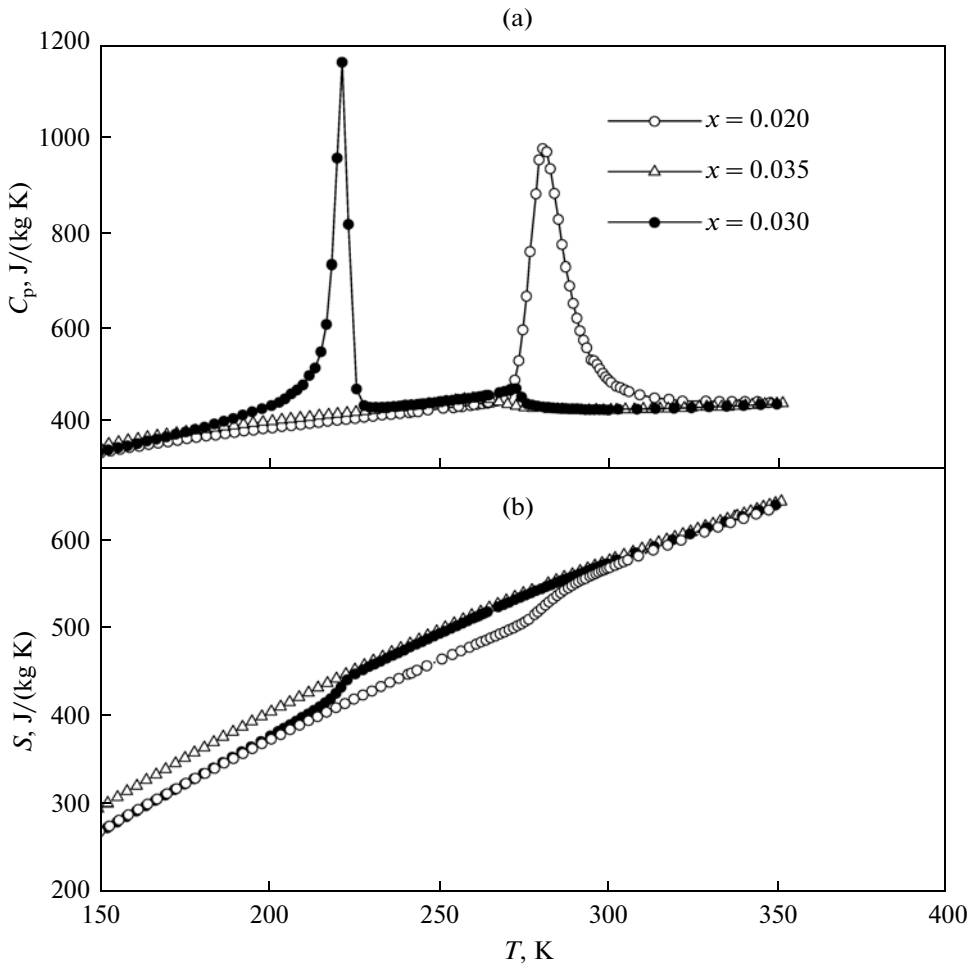

Fig. 7. Temperature dependences of the (a) heat capacity measured upon heating and (b) entropy for the $(MnCo)_{1-x}Ge$ compounds with $x = 0.02, 0.03, 0.035$.

perature dependences of the entropy, which were calculated using data on the heat capacity and standard expression

$$S(T) - S(T_0) = \int_{T_0}^{T} \frac{C_P(T)}{T} dT. \quad (1)$$

where $T_0 = 4.2$ K is the minimum temperature of the heat capacity measurements.

The maximum heat capacity of the compound with $x = 0.03$, which is observed at $T = 221$ K in Fig. 7a, corresponds to the middle of the descending portion of the temperature dependence of spontaneous magnetization. The entropy change upon this transition is 29 J/(kg K). The small anomaly at 270 K corresponds to the Curie temperature of the hexagonal phase. The entropy change observed for the $(MnCo)_{0.98}Ge$ compound upon the combined magnetostructural transition was found to be slightly higher, i.e., 34 J/(kg K). The difference can be due to the higher change of the magnetic contribution to the entropy of the compound with $x = 0.02$.

The entropy change ΔS of these compounds upon isothermal magnetization was studied using the Maxwell's relation. In this case, the field dependences of magnetization of the $(MnCo)_{1-x}Ge$ compositions with $x = 0.01$, 0.02, and 0.03 were measured in fields of to 1.5 T upon heating in a temperature range of 260–310 K at a step 2–3 K. The temperature range covers both the magnetostructural transition for the compound with $x = 0.02$ and the Curie temperature of the compound with $x = 0.03$. Figure 8 shows the magnetization curves for the $(MnCo)_{0.98}Ge$ compound. The entropy changes in applying the magnetic field ΔS_H were calculated by equation driven from the Maxwell' relation

$$\Delta S(H) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (2)$$

Figure 9 shows the field dependences of the entropy change $\Delta S(H)$ at 283 K (the middle of the

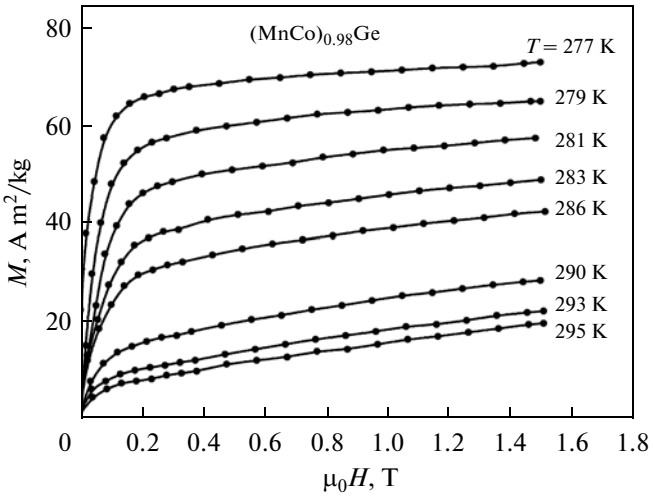

Fig. 8. Field dependences of the magnetization of the $(MnCo)_{0.98}Ge$ compound measured in the range of structural transition at different temperatures during heating.

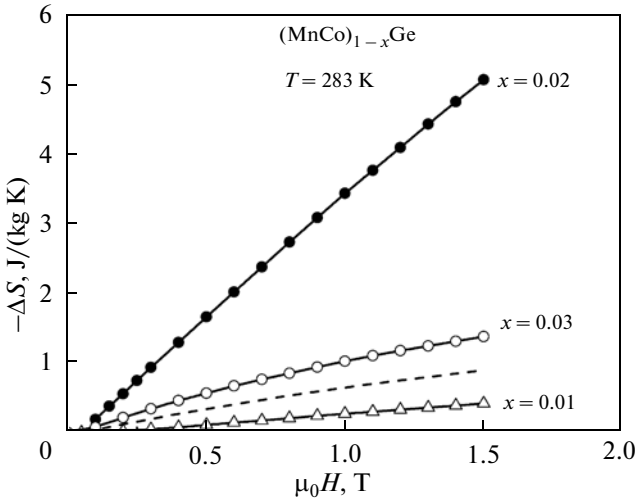

Fig. 9. Field dependences of the entropy change (determined by the Maxwell's relation) for the compositions with $x = 0.01$, 0.02, and 0.03. Dashed line (calculated by Eq. (5)) corresponds to the composition with $x = 0.02$ characterized by equal contents of the hexagonal and orthorhombic phases.

structural transition range for the compound with $x = 0.02$ during heating). It is seen that the maximum entropy change is observed for the composition with $x = 0.02$; in a field of 1.5 T, it is 5 J/(kg K) and is close to values obtained for $MnCo_{0.95}Ge_{1.14}$ [14] and $Mn_{1-x}Cr_xCoGe$ [8]. At the same time the correctness of the obtained result gives rise to doubt.

In the course of first-order phase transition, the relative volumes of phases coexisting in the phase-transition range change. The physical properties of each of phases are determined unambiguosly by magnitudes of thermodynamic variables. Thus, the Maxwell's relation can be applied separately for the H and O phases:

$$\left(\frac{\partial S^{\mathrm{H}}_{0.02}}{\partial H}\right)_T = \left(\frac{\partial M^{\mathrm{H}}_{0.02}}{\partial T}\right)_H ; \quad \left(\frac{\partial S^{\mathrm{O}}_{0.02}}{\partial H}\right)_T = \left(\frac{\partial M^{\mathrm{O}}_{0.02}}{\partial T}\right)_H . \quad (3)$$

Here, $x = 0.02$, which determines the chemical composition of alloy, is used as the inferior index.

Generally speaking, the magnetic properties of the O and H phases in the alloy with $x = 0.02$ in a range of structural transition can differ from those of the O phase of the composition with $x = 0.01$ and H phase of the composition with $x = 0.03$. The formation of hexagonal phase in the matrix orthorhombic phase induces the strained state due to substantial difference between the volumes of the phases. It was shown in [16] that the magnetoelastic contribution to the Curie temperature change dT_C/dP for the orthorhombic and hexagonal phases in the MnCoGe-type compounds is +39 and +12 K/GPa, respectively. Therefore, elastic stresses between the phases coexisting in the sample can lead to the Curie temperature change T_C of the orthorhombic and hexagonal phases by 20–25 and 6–7 K, respectively. However, the structural transition in these alloys is accompanied by disintegration of sample and formation of powder; elastic stresses between phases mainly relax and, in the first approximation, they may be neglected.

In fields below a threshold magnitude of ~2 T, the relative volumes of phases are independent of the applied field, i.e., $d\omega_{\mathrm{H}}/dH = 0$. Therefore, we can write for the whole $(MnCo)_{0.98}Ge$ sample

$$\left(\frac{\partial S_{0.02}}{\partial H}\right)_T = \omega_{\mathrm{H}}\left(\frac{\partial S^{\mathrm{H}}_{0.02}}{\partial H}\right)_T + (1-\omega_{\mathrm{H}})\left(\frac{\partial S^{\mathrm{O}}_{0.02}}{\partial H}\right)_T = \omega_{\mathrm{H}}\left(\frac{\partial M_{0.03}}{\partial T}\right)_H + (1-\omega_{\mathrm{H}})\left(\frac{\partial M_{0.01}}{\partial T}\right)_H , \quad (4)$$

and the entropy change upon isothermal magnetization is

$$\Delta S(H)_T = \omega_{\mathrm{H}}\Delta S_{0.03} + (1-\omega_{\mathrm{H}})\Delta S_{0.01}. \quad (5)$$

Figure 9 shows the expected field dependence (dashed line) of the entropy change upon isothermal magnetization, which was constructed with allowance for the 50% content of the hexagonal phase and 50% content of the orthorhombic phase. It is seen that the entropy change determined in such a way is found to be lower than that determined by Eq. (2) by a factor of 5.

Based on the heat capacity data (Fig. 7) and data on the entropy in the magnetic field, which were obtained by Maxwell's relation while using the $S(T,H)$ dependences plotted [22], the adiabatic temperature change can be easily estimated; when magnetizing the alloy in a field of 1.5 T, it is $\Delta T = 0.28$, 1.7, and 0.72 for the compositions with $x = 0.01$, 0.02, and 0.03, respectively. On the other hand, as follows from

Eq. (5), the value for the composition with $x = 0.02$ is $\Delta T = 0.5$ K, i.e., it is lower by a factor of 3.4.

In order to determine the true magnetocaloric effects for these compounds, direct measurements of the adiabatic temperature change were performed. The inset in Fig. 10 shows the time dependence of the differential thermocouple signal. After switching off electromagnet power (at the time zero $t = 0$), the magnetic field decreases to zero for ~2 s, whereas the time of temperature relaxation of sample was tens seconds. Thus, the measuring conditions can be assumed to be close to adiabatic. The dependences $\Delta T(H)$ are shown in Fig. 10. It is seen that, for compositions with $x =$ 0.01 and 0.03, the measured magnitudes agree adequately with the above data obtained by estimations. The experimental adiabatic temperature change for the composition $x = 0.02$ in fields of up to 1.5 T, i.e., in fields below the threshold field, was found to be several times lower than that obtained by Eq. (2) and to be close to those estimated by Eq. (5).

Let us show why the formal application of the Maxwell's relation can give overestimated data. The magnetization of sample in the range of structural transition is the sum of magnetizations of the coexisting O and H phases

$$M_{0.02}(H,T) = \omega_H M^H_{0.02}(H,T) + (1-\omega_H) M^O_{0.02}(H,T). \quad (6)$$

Taking into account the fact that both the magnetization and amount of coexisting phases change with changing temperature, the temperature derivative of magnetization is of the form

$$\left(\frac{\partial M_{0.02}}{\partial T}\right)_H = \omega_H \left(\frac{\partial M^H_{0.02}}{\partial T}\right)_H + (1-\omega_H)\left(\frac{\partial M^O_{0.02}}{\partial T}\right)_H + \left(\frac{\partial \omega_H}{\partial T}\right)_H \left(M^H_{0.02} - M^O_{0.02}\right). \quad (7)$$

As is seen, an additional contribution to the temperature derivative of magnetization, which is proportional to the difference of magnetizations of coexisting phases and rate of change of their relative volumes with temperature, appears in the range of phase transition. This contribution can be responsible for the difference between the data obtained experimentally and by estimations with Eq. (2). The result obtained agrees adequately with the data given in Fig. 2, which demonstrates that the decrease in the relative volume of the O phase is the cause for the decrease in the spontaneous magnetization of the $(Mn–Co)_{0.98}Ge$ compound in the range of structural transition.

It should be noted that equation close in the form was obtained when studying the MnAs compound [23]. The compound demonstrates the transition of the paramagnetic O phase into the ferromagnetic H phase upon applying the magnetic field higher than the threshold field. In this case, the magnetizations of the both phases slightly depend on the field and can be considered to be unchanged. In contrast to the field dependence of magnetization for the MnAs compound, the field dependence of magnetization for the MnCoGe-based compounds should be taken into account. The magnitude of the temperature derivative of relative volume can be obtained from data on either heat capacity [23] or X-ray diffraction analysis (see Fig. 1b). The additional contribution to the entropy change in a field of 1.5 T, which was estimated in such a way for the $(MnCo)_{0.98}Ge$ compound, is 4.1 J/(kg K). This value allows us to explain the difference between the entropy change upon isothermal magnetization determined by Eq. (5) and that obtained by Eq. (2) when using the Maxwell's relation.

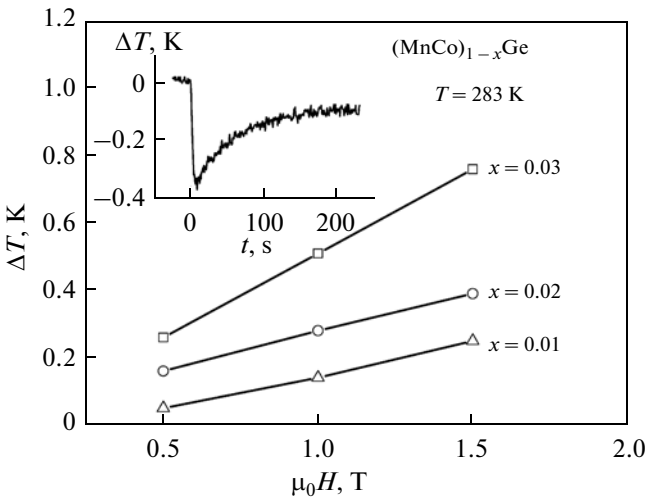

Fig. 10. Field dependences of the adiabatic temperature change for $(MnCo)_{1-x}Ge$ compounds with $x = 0.01$, 0.02, and 0.03. The inset shows the time dependence of differential thermocouple signal after switching off the magnetic field at $t = 0$.

The applicability of the Maxwell's relation for the determination of magnetocaloric effect in the range of phase transitions is discussed actively in the literature. In particular, on the one hand, calculations performed in terms of a model of interacted spins [24] showed that the Maxwell's relation does not work near the temperature of the first-order phase transition. On the other hand, if each isothermal measurement of magnetization is preceded by the heating of sample to paramagnetic state, the Maxwell's relation allows one to adequately determine the isothermal entropy change even for samples demonstrating the high temperature hysteresis near the temperature of the first-order phase transition [25]. In the case of magnetic field sufficient for inducing the first-order phase transition, the Clausius-Clapeyron equation $\Delta H_{cr}/\Delta T = \Delta S/\Delta M$ (where H_{cr} is the critical transition field) can be used. If both the temperature and field can induce the first-order transition, the Clausius-Clapeyron equation

and Maxweel's relation (expressed in finite differences) give close results (see [26] and discussion in [27–29]). If the effect of magnetic field on the structural transition starts only from a certain threshold field, the formal application of the Maxwell's relation can lead to substantial errors.

CONCLUSIONS

The performed studies of the crystal structure, magnetic properties, heat capacity, and magnetocalric effect of the $(MnCo)_{1-x}Ge$ compounds with $x = 0.01$, 0.02, 0.03, 0.035, and 0.05 showed that vacancies present in the 3*d* sublattice affect substantially the temperature of structural transition from the low-temperature orthorhombic phase with the TiNiSi type structure to the high-temperature hexagonal phase with the Ni_2In type structure. The transition in the compound with $x = 0.02$ occurs near the room temperature and is accompanied by an entropy change of 34 J/(kg K). The static magnetic field applied in the range of structural transition, which is higher than the threshold magnitude equal to 2 T, causes an increase in the relative volume of orthorhombic phase having the higher magnetization. When applying the pulsed magnetic field, the threshold field was found to be higher than the aforementioned, whereas the volume change of the orthorhombic phase is less than that observed upon applying the static field. The adiabatic temperature change in the range of structural transition of the compound with $x = 0.02$ in magnetic fields of up to 1.5 T was found to be lower by a factor of 3.4 than that determined from the magnetization curves with the use of the Maxwell's relation. The cause for the difference was shown to be related to the appearance of additional contribution to the entropy, which is proportional to the difference between magnetizations of the coexisting phases and the rate of change of their relative volumes with changing temperature in the range of first-order phase transition.

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